Syngas Chemical Looping: Influence of Supports on Oxygen Carrier Performance

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Abstract

Syngas Chemical Looping (SCL) is a cost effective reforming technology for production of concentrated, high purity hydrogen with in-situ CO_2 capture. One of the crucial parts of SCL technology is the selection of Oxygen Carrier (OC). OC refers to the composite particles used in the SCL process to indirectly transfer the oxygen to the fuel gas from H_2O and/or air through reduction and oxidation reactions. Iron oxide is suited for the SCL process due to its low material cost, favorable thermodynamics for hydrogen generation, strength and high oxygen carrying capacity. However, pure iron oxide is not a good OC; various support materials need to be added to improve reactivity and recyclability of the OC. To explore the most suitable OC which will make the SCL more efficient and more economically feasible, we investigated the properties (reactivity, recyclability and strength) by testing different variations of the OC particles. Iron oxide and various ceramic supports were homogeneously mixed, pelletized and sintered. For reactivity and recyclability tests, the selected pellets are placed in a ThermoGravimetric Analyzer (TGA) to participate in multiple redox reactions using balancing H_2, N_2 and Air. For the strength test, the pellets are crushed using a SHIMPO FGV-100X strength analyzer. A Fix Bed setup tested the particles' physical integrity and structural change. Both the support and concentration of support have a strong and direct influence on the reactivity, recyclability and strength of the OC particles. From the current experimental data, Titanium and Magnesium supports enhance the lifetime of the OC by providing stable redox performance. To identify the optimal OC, more tests need to be done and an OC that can perform well for 100 redox cycles can be synthesized. The OC has a direct

influence on the performance and economical feasibility of the SCL process. The optimum OC will maximize the efficiency of this advanced combustion of Syngas ($CO+H_2$) and enhance in-situ CO_2 sequestration, which can potentially solve the global warming issue associated with fossil fuel utilization.

To my family and friends who I love:

Acknowledgments

Firstly, I would like to express my greatest gratitude to Prof. Liang-Shih Fan for his guidance, and generosity of allowing me to conduct undergraduate research in his multiple phase flow and clean fossil energy conversion lab. My two year stint in the research lab tremendously developed my research, writing, and communication skills. Without the opportunities which Dr. Fan offered me, this thesis would not be possible.

Secondly, I am much appreciative for the guidance and impacts brought by Graduate Associate, Deepak Sridhar. Deepak has overseen and supervised majority of my undergraduate research. He has been a patient and helpful mentor. As a PhD candidate himself, his meticulous and diligent academic style set a role model for me in the future scientific research endeavor. With his insightful guidance, I gained better understanding of the experiments and results.

I would also like to thank Dr. Fanxing Li, Andrew Tong and Ray Kim who helped me developing my research capability, as well as provided me with countless assistance as the research project progresses.

Through my experimental work and interactions with above mentioned researchers in the lab, I reinforced my passion for this career, hoping to become one of them to explore the frontiers of energy research. I was attracted to the rigorous intellectual exercise involved in the process of converting theoretical knowledge into engineering practice, the notion of creation associated with teamwork in establishing the 22 ft tall reactor, and the critical thinking involved in identifying problems and creatively solving them.

My family has always been supportive of my goals in education. Especially my parents, who are both college professors in China, have offered their best to support me both financially and emotionally to studying in the U.S. They are my eternal source of power whenever my academics and life encountering hardships. Without them, I would not even be studying at Ohio State at the first place. I would like also to thank my aunt and my uncle in Houston, and my younger uncle in New Jersey. They took great care of me, and treat me as if I am their own son. It is a shame that my academic performance may not match the amount of efforts they made to me.

Lastly, I would like to thank Yu Pei for always being on my side over the past year. She cooked for me when the research project and experiments turned hectic, and always made my life bright and full of hopes. Her patience, understanding and encouragement have made many hard times bearable.

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Introduction

Environment and Energy

Generation of energy by coal combustion (or other fossil fuels) is accompanied by large emission of CO_2 which is known as a green house gas (GHG). Since the mid 20th century, the carbon dioxide concentration in the atmosphere has increased from 310 ppm in the 1950s to 370 ppm in 2004,[1] and to be projected to 500 ppm in 2050[2].

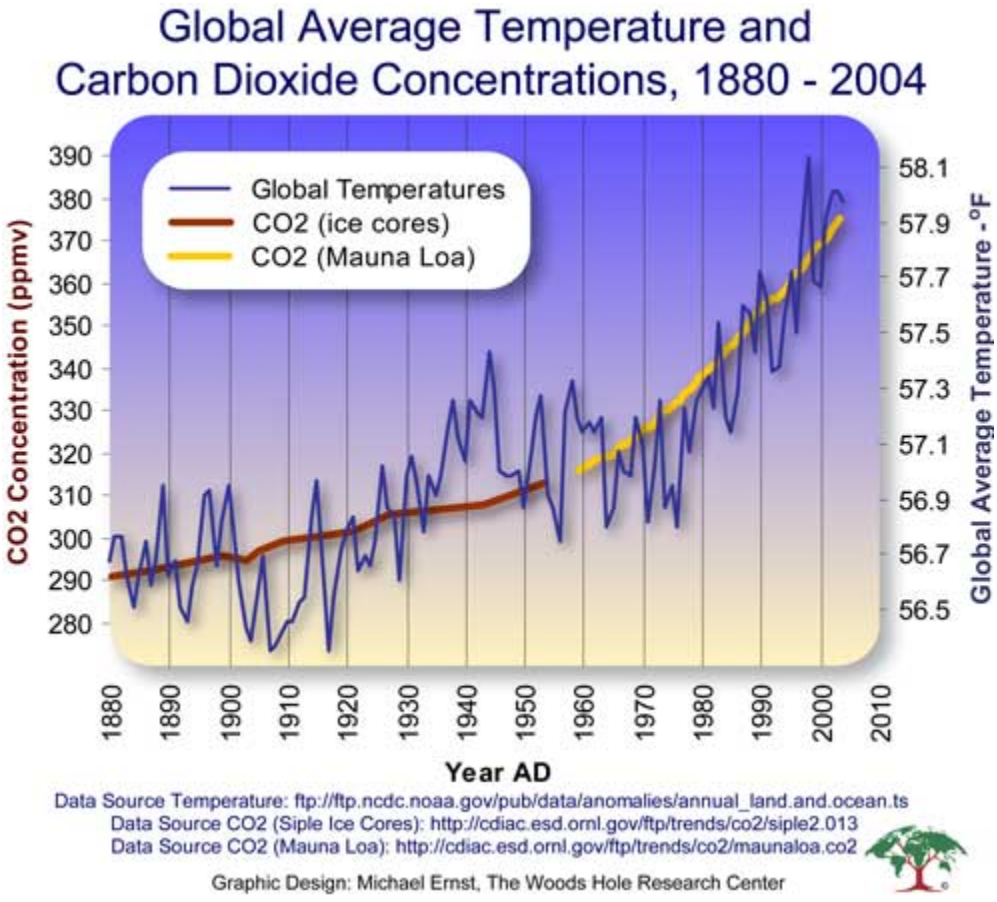

Figure 1: Global Average Temperature and Carbon Dioxide Concentrations 1880-2004[1]

As a GHG, CO_2 is responsible for more than half of the solar radiation emitted back to the Earth's surface. Although disputes still exist in academia whether global warming is totally caused by this increase of CO_2 concentration, we cannot ignore the fact that the average surface temperature of the earth has increased about 1.0 to 1.7 degrees Fahrenheit over the past century.[3] Increment in CO_2 emission, at least in a large part, has caused global warming, which has become a major environmental issue. The change in temperature causes expansion of ocean water and widespread melting of snow and ice cap in the Polar Regions, and leads to rising sea level, which accounts for many adverse conditions both meteorologically and geographically. This increase in CO_2 concentration has also resulted in other environmental and ecological problems, such as decrease in ocean's and natural rain' pH values, loss of wetlands and increased flooding.

Realizing the potential for damage caused by an imbalance in GHG/CO_2, global community has made numerous efforts to reduce or stop anthropogenic CO_2 emissions. With the establishment of Kyoto Protocol in 1997, and the recently concluded Copenhagen Climate Conference and Cancun Climate Summit, multiple attempts across the world have been made to tackle this problem. Legislation to regulate GHG emission appears to be imminent.

Nonetheless, reduction of CO_2 emission rate will remain a big challenge under the current energy consumption structure. According to the World Energy Outlook published by U.S. Department of Energy (USDOE)[4], the demand for energy derived from fossil fuels will continue to increase until the year 2030, with liquid fuel (petroleum), coal and natural gas placed the top three positions by fuel types.

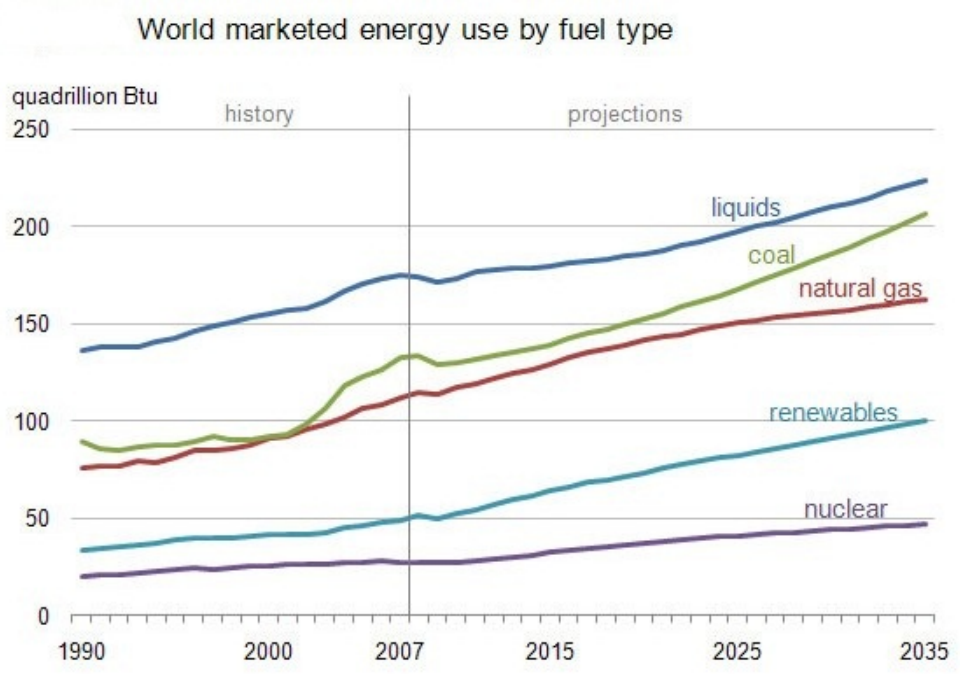

Figure 2: World Marketed Energy Use by Fuel Type[4]

More than half of the world oil reserves and about one third of the world natural gas reserves are located in the Middle East, a region where consistently falls into political instability and terrorist threat. Due to heavy oil dependence, any disruption of oil supply will induce server impacts on world economic growth.

On the other hand, coal reserves are more evenly distributed. United States, Europe, Russia, India and China all have a big share. While the oil price on the world market constantly breaking records, the importance of efficient utilization of coal becomes obvious. Today, the United States, which has one of the world's largest coal reserve known[5], depends heavily on coal to provide energy for the entire nation. About 24.4% of U.S total energy consumption is from burning coal (39.1% from oil and 25.9% from natural gas) [1].

While liquid fuels are crucial for energy consumption in general, coal is the dominate player in electricity production.

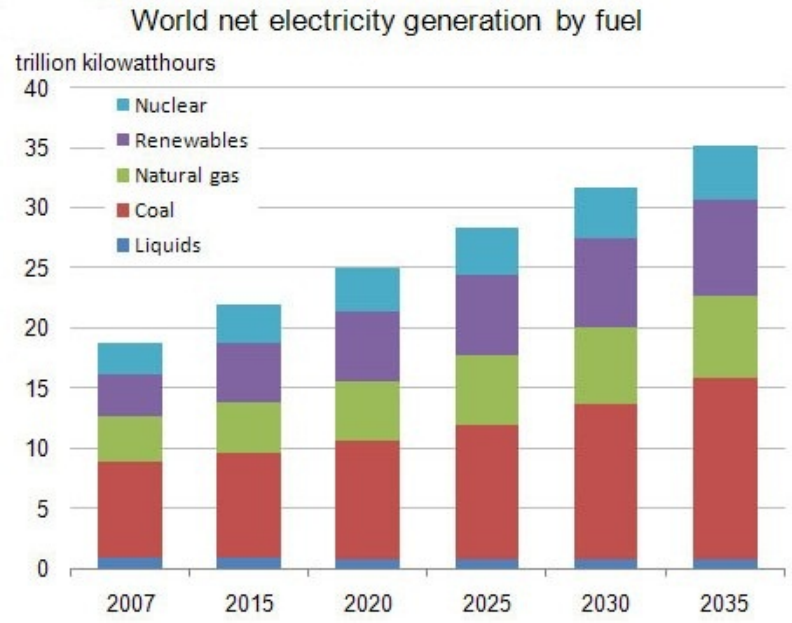

Figure 3: World Net Electricity Generation by Fuel.[4]

Most oil is used for transportation, meaning its consumers are mobile and numerous. Coal consumption occurs in comparatively few locations that are fixed. Thus, coal consumers are the first choice for carbon capture[2]. In the state of Ohio, which is the largest coal energy producing state in the U.S in 2006, 119 coal-fired generating stations in 2005 represents nearly 70% of the state's total electric generating capacity[6] . The usage of coal is expected to increase further because of China's sharp economic growth. China now is the world's largest consumer of coal[7]. Thus CO_2 capture to achieve clean coal utilization and reduced costs for electricity is essential.

In order to comply with the rules established and to reduce GHGs emission, despite all of the political wrestling between different parties internationally, a

technology must be developed to effectively convert coal and other energy sources into electric power and/or various energy carriers while capturing the CO_2 produced.

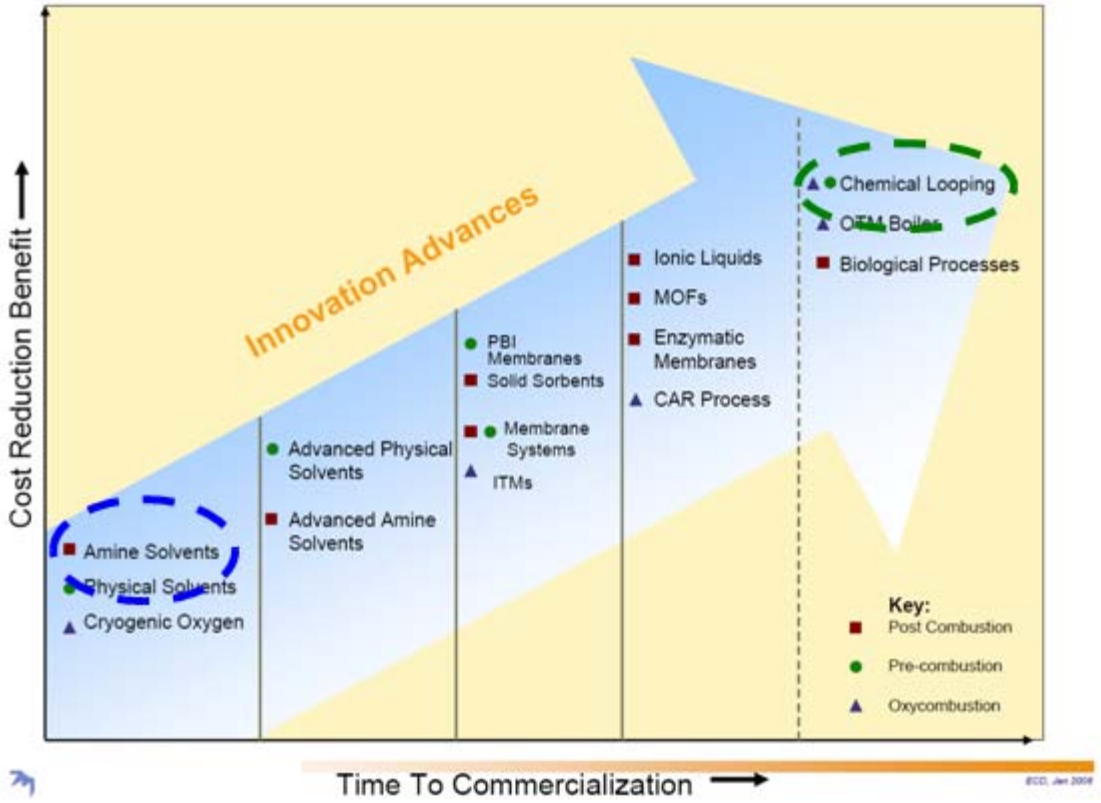

Figure 4: Innovative Options for Carbon Capture. [8]

According to US Department of Energy, National Energy Technology Laboratory (NETL), currently there are many options to achieve carbon capture. (see Figure 4 above). The general trend is that, the higher the cost reduction benefit of CO_2 capture of a technology, the longer the time to commercialize it. One of the latest technologies developed is the Chemical Looping process. It is positioned at the higher bound of the cost reduction benefit trend line, not only because of its nature of oxycombustion and pre-combustion carbon capture, but also due to its capability of generation high purity hydrogen simultaneously.

According to USDOE, hydrogen (H_2) is one of the potential energy carriers which could decrease foreign oil dependence and GHG emission. It can be produced from coal and biomass under certain conditions through a series of chemical reactions. And more excitingly, it could even be produced from water using solar energy, which is carbon free. Even though the current marketability of H_2 remains humble, it still provides us with a promising option, allowing for a potential transition from fossil fuels to renewable energy resources.

Syngas Chemical Looping Process

The Syngas Chemical Looping Process (SCL) is a novel method for the conversion of carbonaceous fuels to both electricity and hydrogen while capturing CO_2 and other pollutants. See Figure 5 below for concept schematics of Chemical Looping.

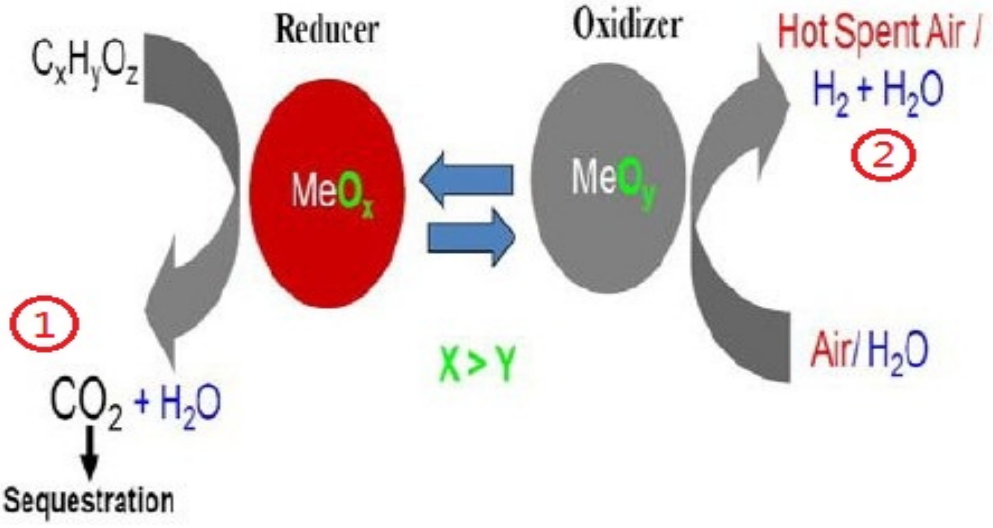

Figure 5: Concept Schematics of Chemical Looping Process [9]

The entire process works by first generating a syngas from either coal or another carbon based fuel through gasification. After preliminary sulfur removal treatment, the syngas then is introduced into the reducer where the metal oxide particles, as a reaction medium, are reduced and consequently transfer the oxygen to the gas. CO_2, H_2O and reduced metal oxide particles are produced. The reduced metal oxide particles then enter the oxidizer, where meets the incoming air (oxygen)/steam mixture. The metal then gets oxidized back to the original state, while the reacted stream consists of H_2 and steam. When streams leaving the reducer and oxidizer both get cooled, water vapor will condense and leave with high purity of CO_2 and H_2 respectively, which could be sequestrated or stored with proper management.

At the heart of the SCL process is an oxygen carrying metal oxide particle, called Oxygen Carrier (OC). OC undergoes redox reactions cyclically to indirectly transform the carbonaceous fuels into useful products, such as high purity hydrogen and heat for electricity production. Previous studies have revealed that iron oxide (Fe_2O_3) can be used as OC.

A more detailed schematic diagram of the SCL reactor developed in The Ohio State University is shown in Figure 6, and Table 1 summarizes the key reactions in SCL process.

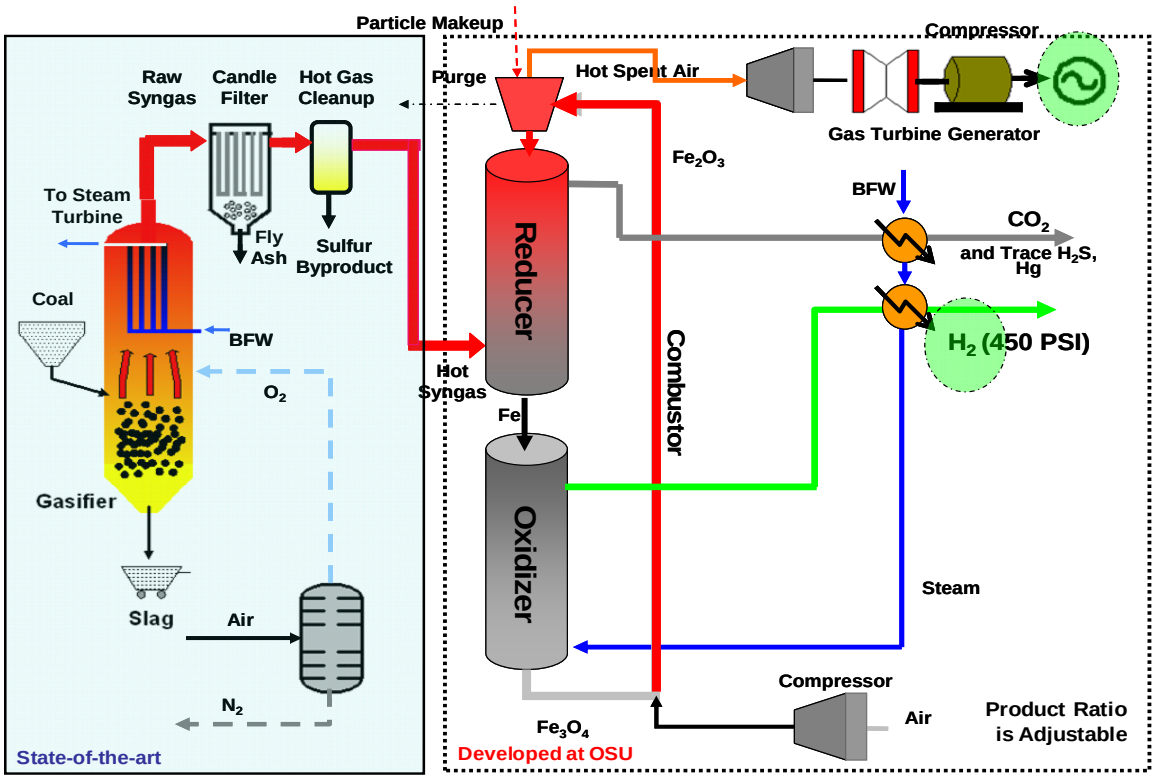

Figure 6: Syngas Chemical Looping Process by Chemical Engineering Department, The Ohio State University

Reducer:
$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$ $\quad FeO + CO \rightarrow Fe + CO_2$
$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O$ $\quad FeO + H_2 \rightarrow Fe + H_2O$
Oxidizer:
$Fe + H_2O(g) \rightarrow FeO + H_2$ $\quad 3FeO + H_2O(g) \rightarrow Fe_3O_4 + H_2$
Combustion Train:
$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 + Heat$
Overall Reaction : $C_xH_yO_z + H_2O/O_2 \rightarrow CO_2 + H_2 + Heat$

Table 1: Key reactions in SCL process.

As illustrated in above Figure XXX, the combustion of syngas and generation of H_2 take place in two different reactors (the reducer and oxidizer), therefore the separation of CO_2 is inherent, which means no additional separation is needed. Compared to the conventional coal fired power plants where CO_2 separation is required, SCL totally cuts the cost for this step and hence is economically feasible. More importantly, by sequestering CO_2, the overall process is carbon neutral to the atmosphere and could potentially achieve zero emission.

The implications of SCL are broad.

First, the SCL process is a clean coal process because of its potential for zero emissions of CO_2 and other pollutants. In the past, clean coal energy had been economically infeasible because of high parasitic energy requirements for separation of various pollutants, such as CO_2, sulfur and mercury, but with this technology, clean coal becomes feasible.

Second, because OC reacts with syngas and other carbonaceous fuels, the feed to the system is not limited to coal, and could be extended to many other sources, for example methane (natural gas). This versatility enables SCL technology to be applied to biofuels, which transforms it to a robust alternative energy process.

Third, as mentioned before, SCL has the ability to generate high purity H_2. This is a huge bonus other than generation of electricity. This ability, if properly modified, could even be used for sole production of hydrogen. The hydrogen generated is now 99.97%[10] pure which is suitable for many applications, for example the Fischer-Tropsch synthesis, without further processing.

Oxygen Carrier Particles

The iron-based OC in reducer/oxidizer/combustion train cycle is the crucial reaction medium for the SCL process, and therefore received the most attention in the research. The gasifier could be approximated by using CO/H_2 mixtures to represent syngas, but this study investigated the use of hydrogen solely for the reduction of Fe_2O_3.

While the SCL process itself offers promising future for carbon dioxide sequestration and the possible cogeneration of hydrogen and electricity, the OC particle determines how successful this process can be. Several metal oxides (for example, Fe_2O_3, NiO, CuO, CoO) have the oxygen carrying ability. In choosing a suitable OC, however, several points must be kept in mind.

First is the health and environmental impact. Amongst the four metal oxides mentioned above, Ni^{2+} is a known carcinogen; Co^{2+} also has adverse effect to human health. Although these two have been widely used in chemical industry for catalyst purposes, they are at odds with the "green, clean and environment-friendly" principles of SCL. Fe^{2+} and Fe^{3+} irons are important for human body function. See Table 2 below.

	Fe_2O_3	NiO	CuO	CoO
Cost	+[1]	–	~	–
Oxygen Capacity[2] (wt %)	**30**	**21**	**20**	**21**
Thermodynamics - reduction[3] **steam oxidation**	+ +	+ ~	+ –	+ +
Kinetics/Reactivity[4]	–	+	+	–
Melting Points	+	~	–	+
Strength	+	–	~	~
Environmental& Health	~	–	~	–

1. +: positive; –: negative; ~neutral
2. Maximum possible oxygen carrying capacity by weight, pure basis; achievable (actual) oxygen carrying capacity is affected by a number of factors including the maximum oxygen carrying capacity, support percentage, thermodynamic properties, and reactor design
3. Capability to fully oxidize C, CO, H2 to CO2 and H2O according to thermodynamic principles
4. Reactivity refers to the rates of the reactions between metal oxides and syngas (CO and H2)

Table 2: Comparison of various metal oxides as base OC

Moreover, the market prices for NiO and CoO are much more expensive than the other two. In the future when SCL is scaled up to industrial level operation, depending on the throughput and power of the plant, large amount of OC particles is needed. An iron based OC will be very low in cost and easy in scale up of synthesis procedure.

Second is the reactivity. Reactivity of OC refers to the oxygen carrying ability. The higher the reactivity, the larger amount of oxygen can be transferred in one cycle with same amount of OC. Iron has a +3 oxidation state while nickel has +2. With similar atomic weight, iron has a larger oxygen capacity. Moreover, tests have shown that nickel is only suitable for heat generation whereas iron can also be used to produce hydrogen.

Third is the recyclability. In SCL, OC must undergo numerous redox cycles and maintain its reactivity. This is crucial because otherwise the SCL reactor will need to stop frequently and large amount of OC replacement will be needed to maintain the overall throughput. This will decrease the production time and increase operation cost.

Last is the durability / particle strength. The SCL system is a giant fluidized bed reactor. OCs are numerous small pellets of diameter less than 3 mm, and they are directed to undergo the redox cycle. Motion in the reactor will certainly cause attrition of the OC pellets, since the pellets contact with each other and the reactor inner wall, and hence abrased. In addition, OC pellets need to have suitable heat capacity and high melting points. OC pellets with these high qualities increase their service time, hence reduce cost.

Based on the 4 properties listed, iron oxide is chosen to be the base of OC. However, pure Fe_2O_3 is not a suitable OC. Therefore, other metal oxides, ceramics and clay materials, such as TiO_2, MgO, Al_2O_3, Kaolin, Bentonite, etc need to be added as support to enhance the performance of the OC.

The project involves making different batches of particles with Fe_2O_3, and TiO_2, MgO, Al_2O_3, Kaolin, Bentonite and other materials as support. We then will investigate characteristics of OC mostly related to SCL process. The primary objective is to investigate 3 main characteristics (reactivity, recyclability, and strength) of Fe_2O_3 particles with various support compositions; to select the most efficient and economical combination to enhance Oxygen Carrier performance; and to modify the SCL process and to improve its overall efficiency of achieving clean coal utilization.

Experimental Methodology

Particle Making and Pelletization

The SCL process involves large amounts of particles to be used at one time. We will mainly focus on a mechanical mixing method to prepare for the particles, as it is the easiest to perform and most cost effective compared to other methods such as Impregnation and Sol-Gel. Mechanical mixing may not achieve the same level of homogeneous mixing as impregnation and sol-gel do, but previous studies have proven that the level of inhomogeneous mixing by this method has insignificant influence on the overall particle reactivity. Mechanical Mixing thus becomes the most suitable method in terms of time limit and economical feasibility, especially when comes to scale-up synthesis procedure.

The compositions of the particles vary, with Fe_2O_3 being the main components combined with different supports (TiO_2, MgO, $Al2O_3$, Bentonite, etc) of various percentages. For research purposes, 50 grams of mixed powder is produced for each combination of Fe_2O_3 and support. This amount is sufficient for producing more than 30 pellets of 3 mm diameter.

To prepare the usable pellets, there are 3 main steps, namely particle making, pelletization, and sintering.

To begin, pure powder of each chemicals are sieved using the Autosieve, with about 1.5 lbs of ½" diameter carbon steel balls as grinding media. The autosieve operates by shaking sieves in the lateral direction with an arm which taps the lateral movement. An image of the autosieve and grinding media are given below in Figure 7. The steel

media promote attrition of the agglomerated powder, to help homogeneous mixing in the flowing steps. As soon as the powders fall below of the screen spacing of the sieve, they fall to the next sieve where the process repeats itself. The process repeats until all the powders are finely grinded.

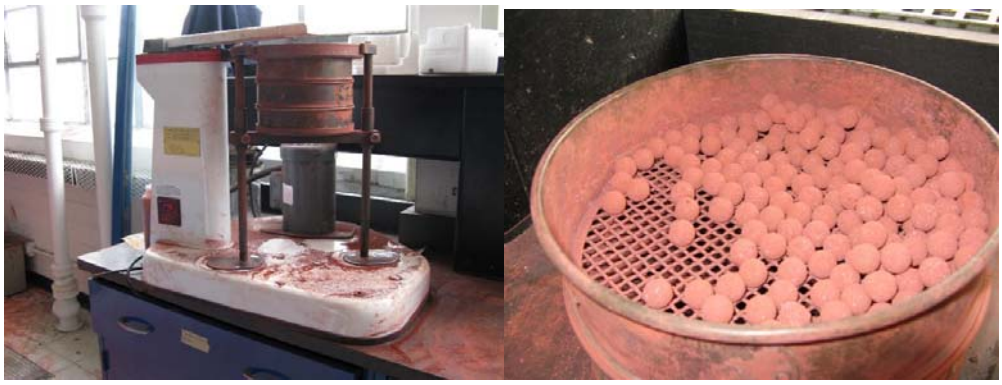

Figure 7: Autosieve and grinding media

The mixing was done using the Rotating Drum Mixer (Figure 8 below), and by adding 4 wt% Magnesium Stearate powder as diluents to lubricate flow of powder and help homogeneous mixing. After mixing is complete, the powders are well mixed and ready for pelletization.

Figure 8: Rotating Drum Mixer

The powders are collected and pelletized to 3 mm diameter pellets using the bench top pelletizer. 30 pellets were produced for each unique combination of Fe_2O_3 and support. Left over powders are put into shelf, and not exposed to ambient air. This is to prevent moisture from reaching the powder and forming agglomerates.

In case of large production of pellets for sub-pilot scale SCL plant, the larger pelletizer was used. The large pelletizer has a hopper which stores the powder and feeds into a rotary die set. The rotary die has a matching punch set which presses the powder into a pellet. For the larger pelletizer, clogging is a concern, therefore proper and homogeneous mixing becomes very important.

Once the pellets are made, they are put into ceramic crucibles and sintered in oven at 900 ˚C overnight. The sintering process increases the particle strength tremendously, and reduces the attrition rate of particles when they are moving in the fluidized bed. Such high durability is necessary for the OC operating in the SCL system. One setback of the sintering process is that the OC particles will lose some of their reactivity due to the bonding structure change at high temperature. However, strength of the particle is more important for the overall SCL system.

Reactivity and Recyclability Testing (TGA)

A ThemoGravimetric Analyzer (TGA) was used to measure the effects of varying support in the redox reactivity of the composite particle. The TGA itself is capable of reaching temperature up to 900 ºC. The TGA itself will raise the sample temperature up to 900 ºC under normal atmospheric pressure. The TGA is also connected to a gas panel via three Teflon tubes. The panel is then connected to three gas cylinders containing nitrogen, hydrogen and air.

A computer software is used to control the furnace and the gas flows (N_2, H_2 and Air). H_2 is used for reduction to occur, while air is used for oxidation. Periods for reduction and oxidation were varied (ranging from 20 to 60 minutes. N_2 will be used as a flushing gas between each stage. 5 cycles of redox reaction were performed with each sample to see if the particles still retain oxygen carrying capability after multiple cycles and are recyclable. The program used for both gas flow and temperature control is Pyris.

A quartz sample holder was used to hold the samples during the experiments. The TGA itself has a glass tube with approximately a 15 mm inner diameter which encases the reactant gases and is water cooled to protect the balance. The furnace wraps around the glass tube to provide heating to the sample and reactant gases. Figure 9 shows the setup of the TGA.

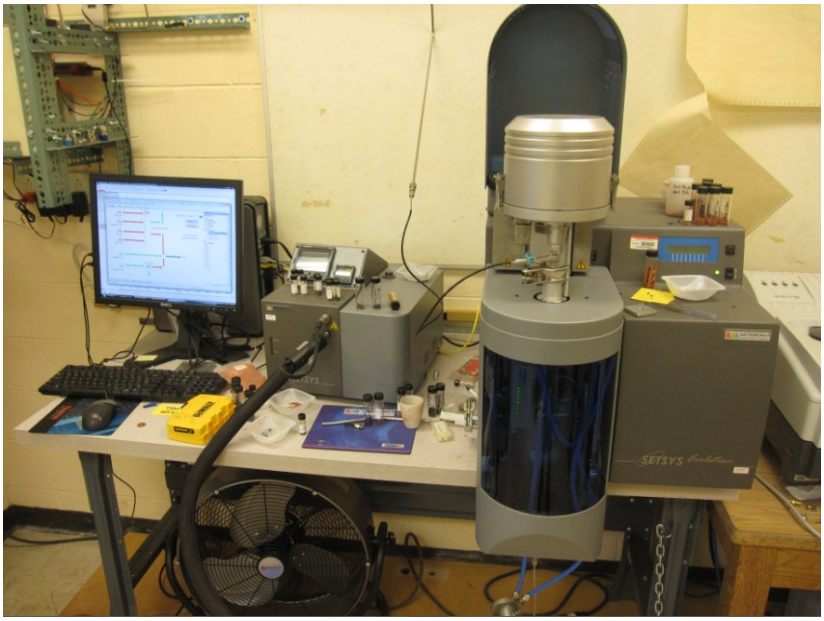

Figure 9: ThermoGravimetric Analyzer setup.

In the operation of the TGA, the nitrogen gas was allowed to flow during the warm up period. This is to prevent the sample to react with air under high temperature. After the appropriate temperature had been reached, the hydrogen was switched on to allow the

reduction to occur. The hydrogen flow was set to be 1L/min at STP (25 ˚C and 1 atm). After the reduction is done, 5 minutes of nitrogen flushing period was introduced to drive away the left hydrogen and set ready for oxidation.

For one sample, the total experiment time includes:

1. Initial warm up (20 min)
2. Reduction (20 min) x 5
3. Flushing (5 min) x5
4. Oxidation (20 min) x5

Total = 245 min ~ 6 hrs

Strength & Structural Integrity (Fixed Bed Testing)

As described in the previous sections, the strength of the particle plays a pivotal role in the selection of an oxygen carrier for chemical looping processes. It is expected that the strength of the particle decreases as the number of redox cycle increases. To confirm this observation, sintered pellets of the same composition underwent 20 redox cycles and their strength and volume before and after the experiment were compared. The strength and volume measurement cannot be obtained from one pellet; multiple pellets were utilized for obtaining this data. This made the TGA test inconvenient, since only 1 pellet could be fit in to the TGA at one time. For this purpose, fixed bed testing was used (see Figure 10 below for set up).

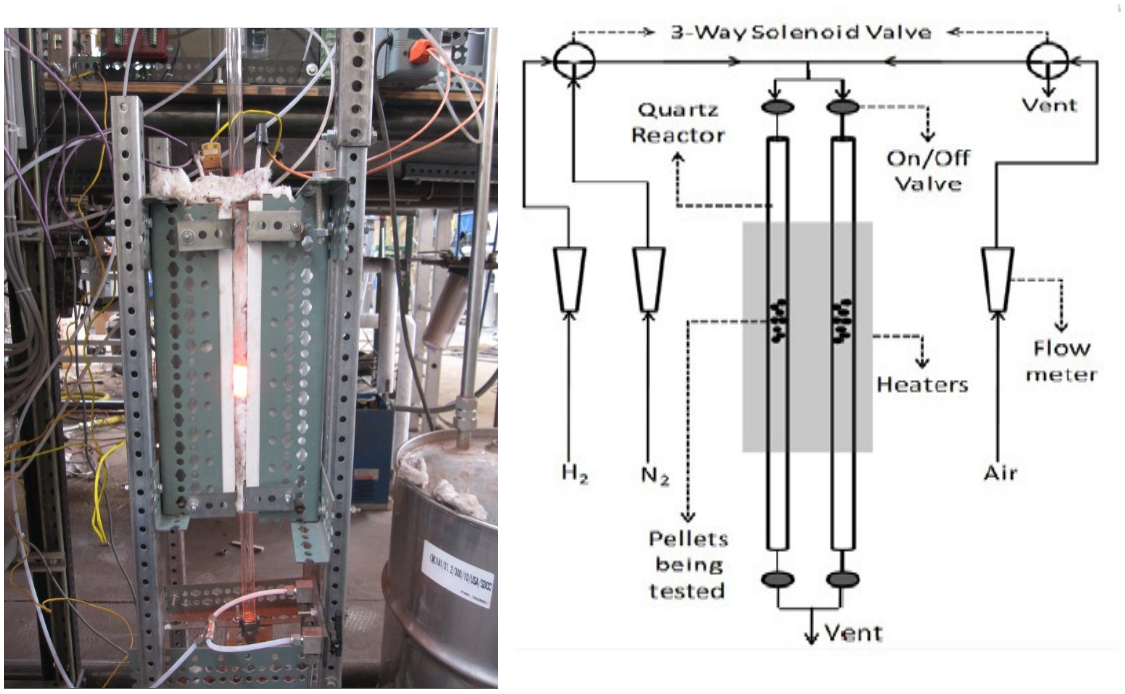

Figure 10: Fixed Bed Setup for multiple pellet redox testing[11]

5 sintered pellets are placed inside the fixed bed (quartz tube reactor) and heated to 900 C under nitrogen atmosphere. 2 reactors can be used simultaneously, such that Then multiple redox reactions are performed. A constant flow of 5 liter/min of N_2 is used through the flushing period. During the 20 minutes reduction stage, 2 liter/min of H_2 is introduced. During the 20 mins oxidation stage, 4 liter/min of air is introduced. A 5 min flushing time is introduced between the 2 stages. The flow rates here are total flow rates and the flow in the individual reactors is close to 50% of the total flow rate. After the experiment, the reactor is cooled under N2 atmosphere and the particles are collected for strength and shape testing.

For the strength test, the pellets are crushed using a SHIMPO FGV-100X strength analyzer. See Figure 11 below.

Figure 11: Strength Test Analyzer

The pellets are crushed perpendicular to the cylinder axis as it is expected to provide the lowest crushing strength of the particle, since this lowest crushing strength is the limiting factor of the attrition rate of the particles in the moving bed. The structural change is then measured using a Vernier caliper and the volume change is documented.

Experiment Results and Discussion

Reactivity & Recyclability (TGA Testing)

The TGA yields a graph of mass of the particle against reaction time. By using the following equations, weight percentage change of the particle is calculated.

$$Wt\% = \frac{M_{current} - M_{initial}}{M_{initial}} \times 100\%$$

Equation 1: Weigh Percentage Change of the Particle

And a sample weight percentage change graph is shown below in Figure 12.

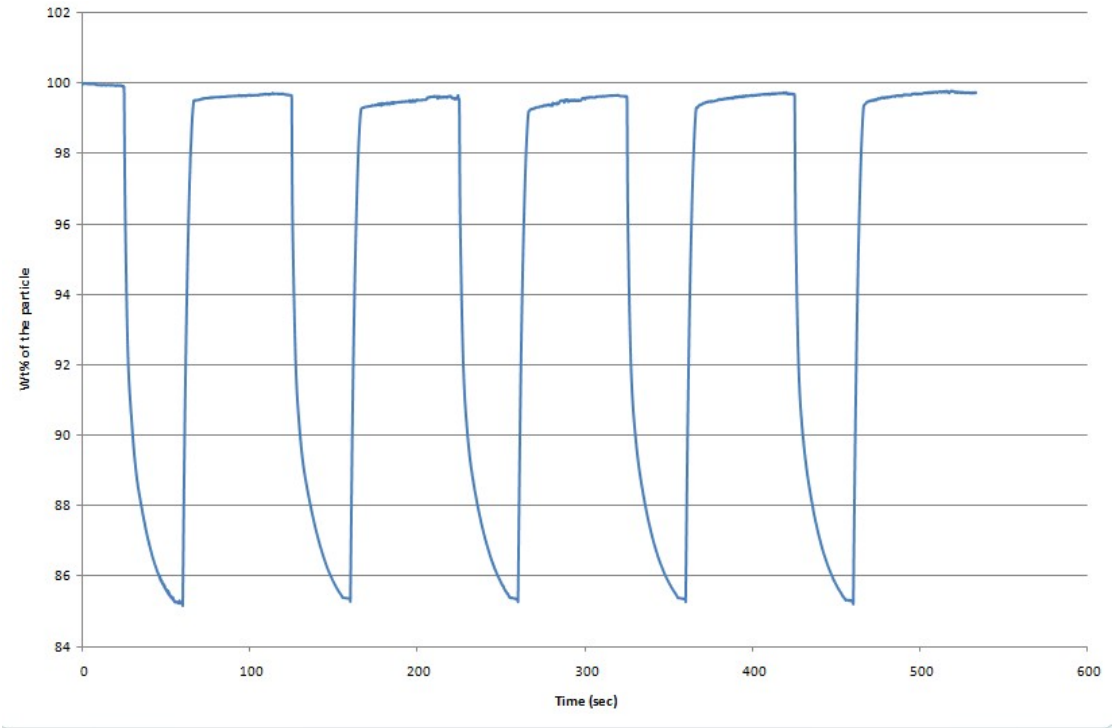

Figure 12: Weight Percentage Change of Particle for Reactivity and Recyclability Test. (sample)

Since this is a redox reaction, the weight change is purely caused by the loss of oxygen from the metal oxide. Then the lost oxygen is utilized in the SCL process to achieve indirect combustion of the incoming carbonaceous fuel. Therefore there is a linear relationship between the wt% change and the oxygen capacity. The greater the weight percentage change of the particle, the more oxygen can be utilized. Therefore the particle has strong oxygen capacity, or simply called reactivity.

At the same time, the particle must undergo multiple cycles and still retain its oxygen capacity. Figure 13 below shows the oxygen capacity of pure Fe_2O_3.

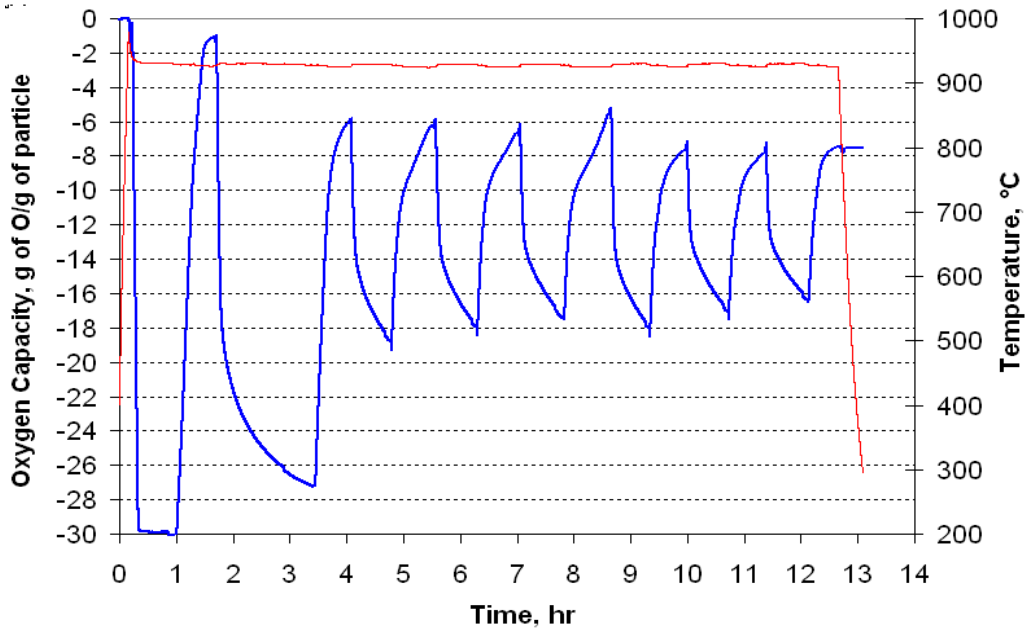

Figure 13: Oxygen Carrying Capacity of Pure Fe2O3

As we can see from the graph, the oxygen capacity of the pure Fe_2O_3 pellets decreased dramatically after two cycles, which means that the pellet has very poor recyclability. A good pellet is expected to undergo at least 100 cycles of redox reaction and still maintain its reactivity in a decent level to make the entire SCL process energetically and

economically feasible. As previously mentioned, support materials need to be added in, to increase the reactivity and recyclability of the composite pellets.

Various literature searches shows that various metal oxides, ceramics and clays materials also possess the oxygen capacity suitable for SCL process. Selected clay materials (including kaolin and bentonite) and non-clay materials (including: TiO_2, SiO_2, MgO, Al_2O_3) are mixed with Fe_2O_3 particles, and their oxygen capacity is tested. (Due to restriction of the proprietor's contact, the exact composition and identification of each pellet are not to be revealed).

To calculate the oxygen carrying capacity of each support-added pellet, first we calculated the theoretical oxygen carrying capacity, meaning that based on the expected concentration we obtained the maximum amount of oxygen can be donated by the particle (assume complete reduction and oxidation). Then from the TGA test, we obtained the actual amount of oxygen donated by the pellets. So the oxygen carrying capacity is the ratio of actual value to the theoretical value. Literarily, the actual value should not exceed the theoretical value (maximum value by calculation), however there are 2 possible reasons accounted for this discrepancy:

1. The pellets are not well mixed. Mechanical Mixing is not a perfect mixing method for homogeneity. It is possible that the amount of supports added in is not of expected value, such that the amount of oxygen content of the Fe_2O_3 in each pellets are not in agreement with theoretical values.
2. In the calculation of theoretical oxygen carrying capacity, we assumed that the added support will not undergo redox reaction. However, later we confirmed that the supports did undergo redox reaction too since some of them are metal oxides too. This will contribute more oxygen for the system, thus increase the actual oxygen value from the experiment.

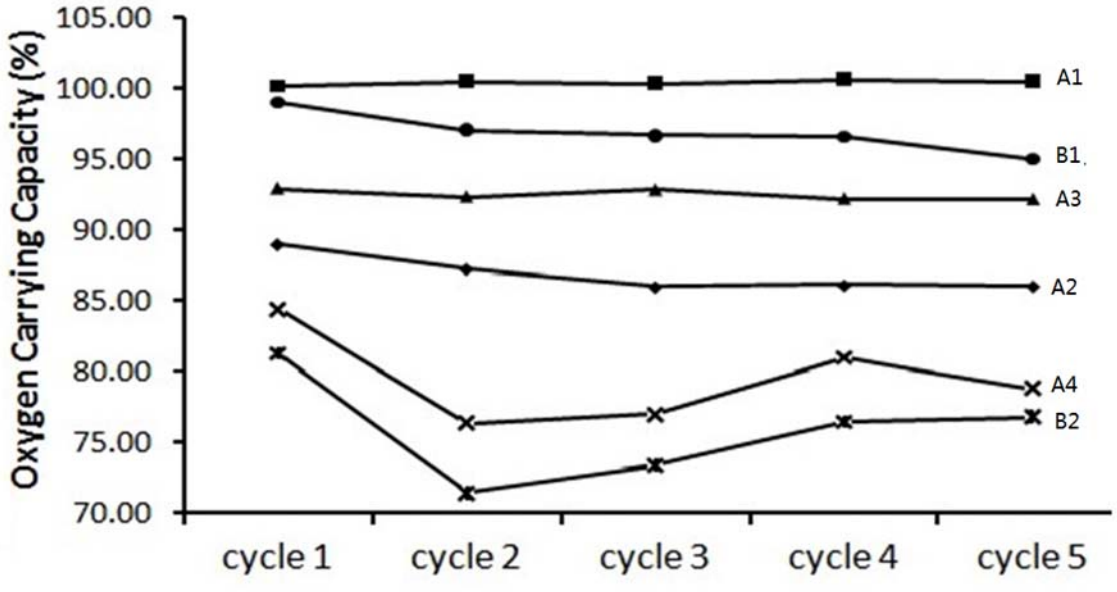

Figure 14: Oxygen capacity of single support on Fe2O3 based pellet.

Figure 14 above shows the influence on pellet's oxygen carrying capacity when each support material is added individually. As we can see, A1 pellets have the highest OC capacity, followed by B1, A2, which all have OC capacity above 90%. A4 and B2 have OC capacity lower than 80% after 1 cycle, which indicate they are not suitable to be added as the single support.

More importantly A1, B1 and A2 demonstrated relatively consistent OC capacity for 5 redox cycles, which indicates good recyclability. A1 is the best amongst them, followed by A2. The B1 pellet, though its OC capacity didn't fluctuate much for the first 5 cycles tested, shows a graduate decreasing trend. This rises up a concern whether kaolin pellets can last for longer testing, say, 100 cycles to meet requirements for actual SCL operation. The A4 and B2 particles show big fluctuation in their OC capacity for the first five cycles, therefore they have bad recyclability, and again, they are not suitable to be added as the single support.

Combine the results of reactivity and recyclability tests, A1 and A2 are proven to be the best single-added support.

We also noticed that when varying the Fe_2O_3 base content in a pellet, same support material will show different reactivity and recyclability. Figure 15 below shows how the OC capacities of each support-added pellet vary when F_2O_3 content is increased by 10wt%.

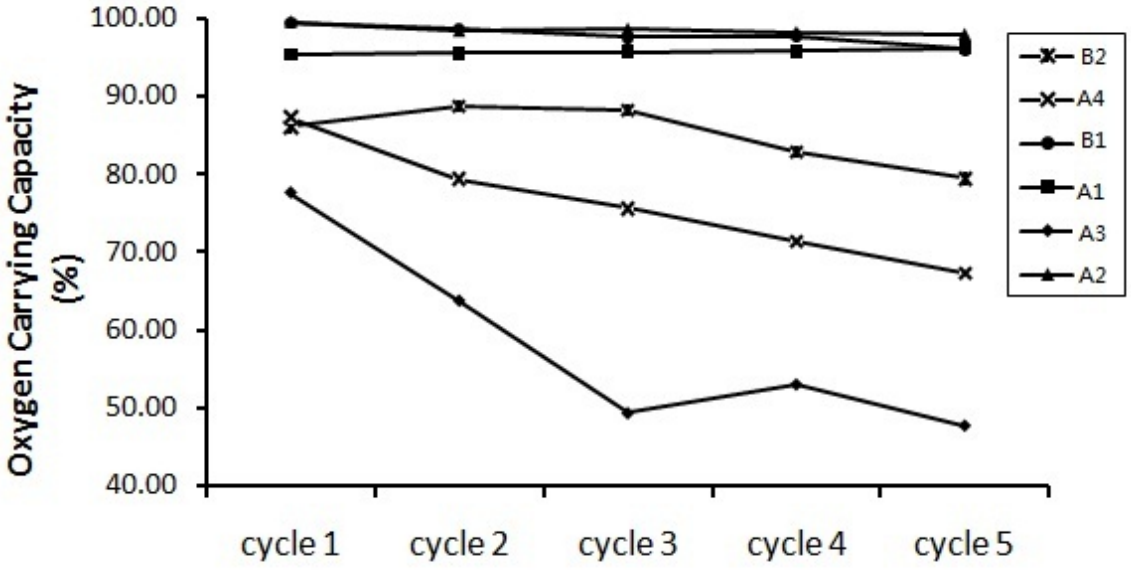

Figure 15: Oxygen capacity of single support on Fe2O3 based pellets.

(Increased Fe2O3 content by 10%)

As we can see from the graph, A3, A4 and B2 pellets show obvious decrease in reactivity over 5 cycles, while A1, A2 and B1 retains high reactivity. A1 even shows a slight increase in reactivity over the 5 cycles, and kaolin, same as previously said, showed a slight decrease. Therefore, whether it can be sustained for 100 cycles remains a question.

Therefore, from results of single-added support pellets, A1 and A2 are the most suitable in terms of reactivity and recyclability.

In order to further investigate the supports, two supports form a combination and then are added in to the Fe_2O_3 based particles. For clearer comparison, supports are categorized into 2 parts, clay (with Kaolin and Bentonite) and non-clay (without Kaolin and Bentonite). Figure 16 below shows the OC capacity of non-clay support mixture in Fe_2O_3 pellets.

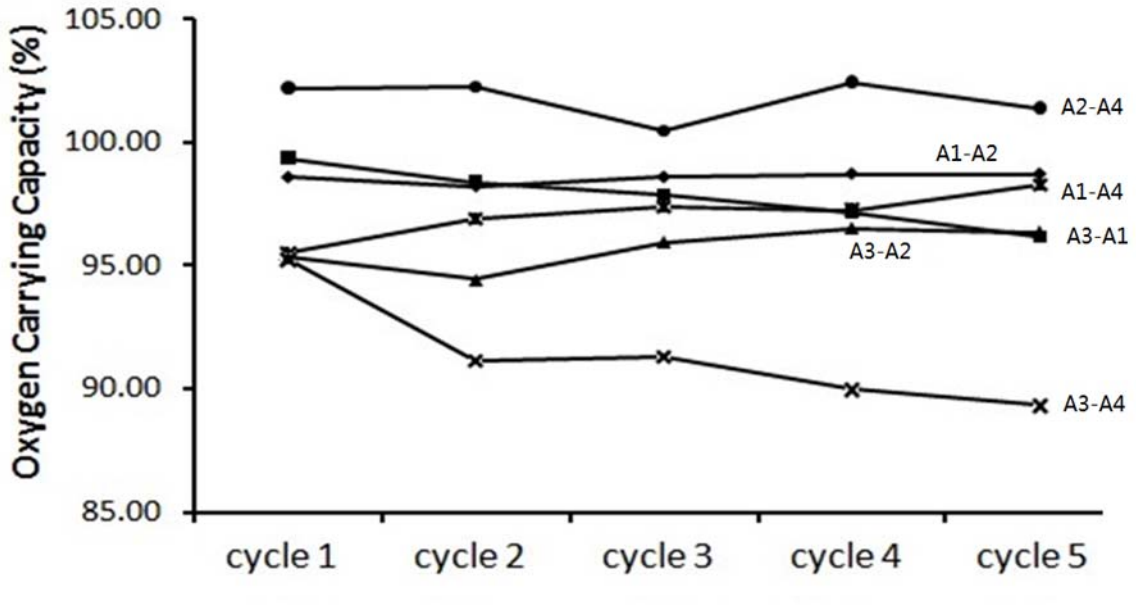

Figure 16: Oxygen capacity of non-clay mixed support on Fe2O3 based pellet.

All the support mixtures show a relatively high reactivity above 90%. However, the A3-A1 and A3-A4 combinations both show a decreasing trend in reactivity, suggests that A3 is not a good support. Even though A3 provides high OC capacity, it will not last long. A3-A4 and A1-A2 show increasing in OC capacity for the 5 cycles, indicating good recyclability. The most stabilized combination is A1-A2. As in agreement with previous experiments, A1 and A2 are the most suitable support material in terms of reactivity and recyclability.

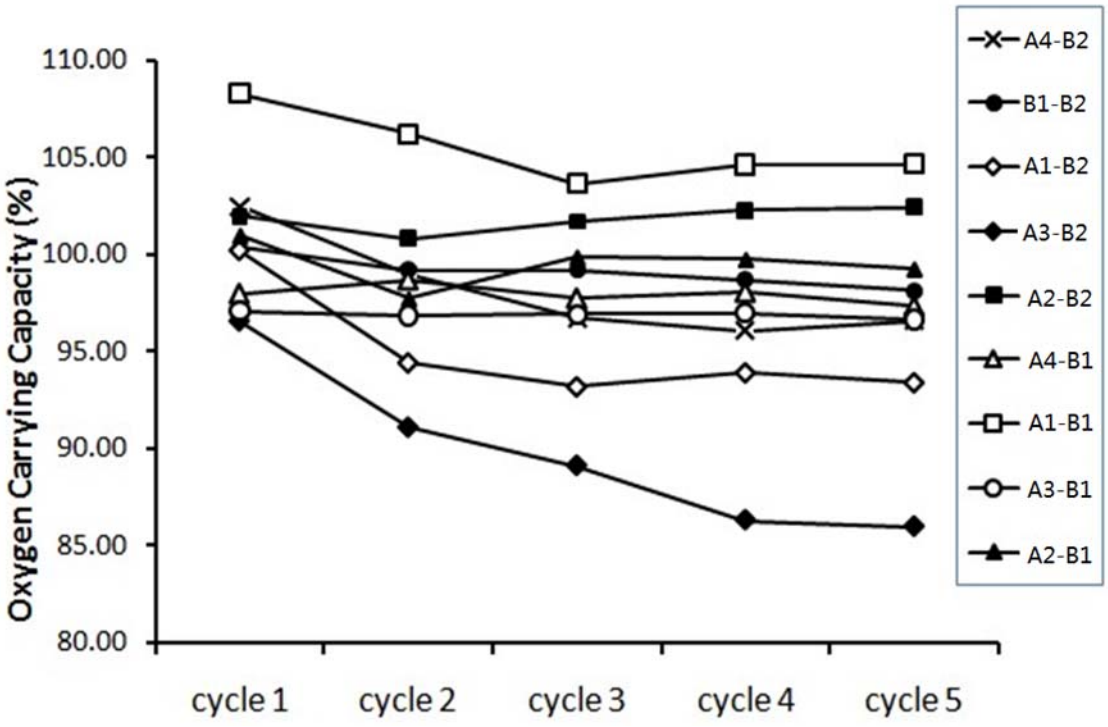

Figure 17: Oxygen capacity of clay mixed support on Fe2O3 based pellet.

When each metal oxide mixed with clay materials, the OC capacity results are shown in Figure 17 above. Majority of the pellets shows a stabilized OC capacity over 5 cycles, with a few being exceptions. A2-B2 combination shows an increase in reactivity, while A1-B1 and A1-B2 show decrease in reactivity. This suggests that clay materials, with increased reactivity, may reduce the overall recyclability of the pellets.

The size of the particles also plays an important factor influencing OC capacity. Figure 18 below shows the results obtained for same composition of particles, both in powder form and 3 mm diameter pellets form.

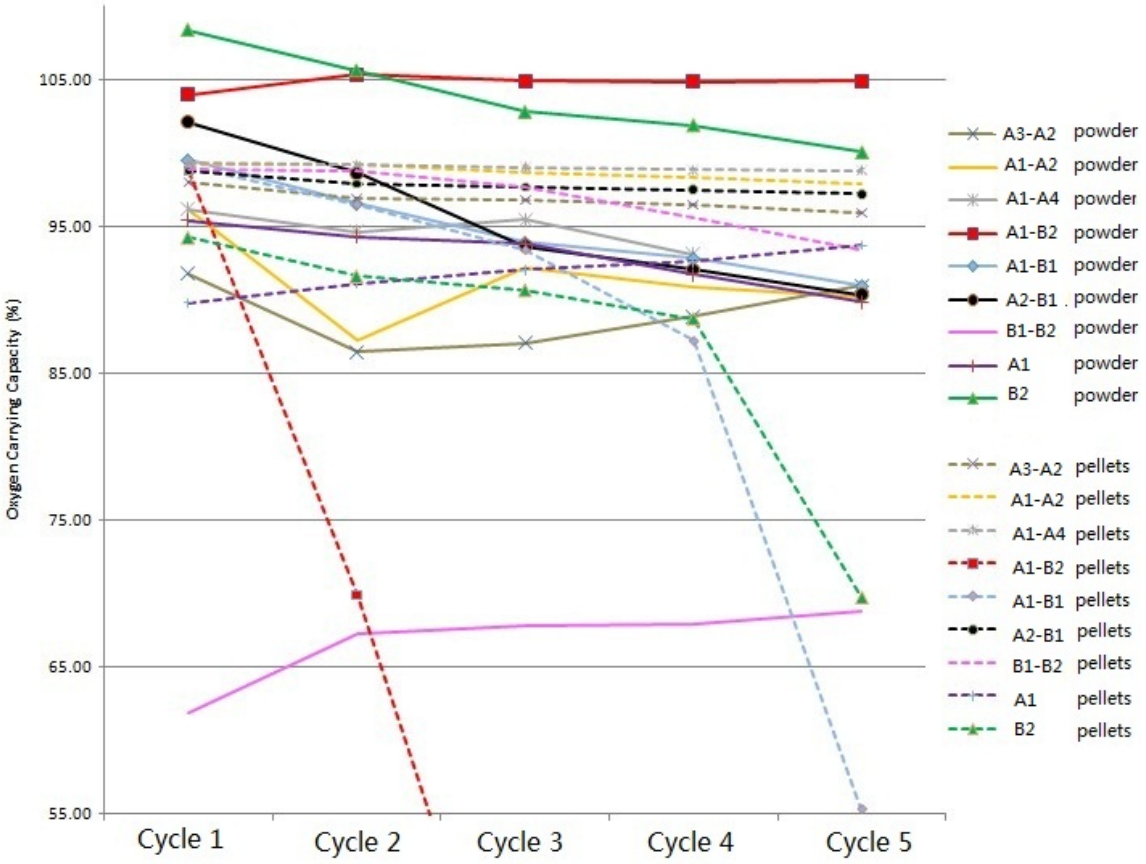

Figure 18: Oxygen Carrying Capacity of various composition particles, in powder form and pellet form.

The results can be summarized to Table 3 below:

(pellets)	A3-A2	A1-A2	A1-A4	A1-B2	A1-B1	A2-B1	B1-B2	A1	B2
Reactivity	+	+	+	-	-	+	+	+	-
Recyclability	~	~	~	-	-	~	-	~	-
(powder)	A3-A2	A1-A2	A1-A4	A1-B2	A1-B1	A2-B1	B1-B2	A1	B2
Reactivity	+	+	+	+	+	+	-	+	+
Recyclability	-	-	~	+	~	-	-	~	-

Table 3: Reactivity & Recyclability Test Results for multiple supports on Fe_2O_3, Powder vs. Pellets

The table clearly shows that particles in powder form have higher OC capacity as well as higher recyclability, while particles in 3 mm pellet form show a weaker recyclability for certain combination. These differences could be accounted for following reasons.

1. Powder particles have larger surface to volume ratio, meaning larger reaction area in the SCL reactor. Oxygen exchange rate will be higher, resulting a higher oxygen carrying capacity.
2. Powder particles are better mixed, meaning the Fe_2O_3 base is more homogeneously mixed. The support materials will be more evenly distributed in the particle under testing, and the overall reactivity is higher.
3. Pellet particle will undergo expansion after certain redox cycles, thus losing its structure integrity. The oxygen exchange rate, therefore, also decreases along with the change of particle structure.

Although powder particles have advantages in reactivity and recyclability, they have a critical disadvantage, which is the clogging issue. Since the entire SCL reactor system is a fluidized bed, powder particles tend to clog on the inner wall of the reactor as well as any junction or turning point of the system. This is bad because once the agglomerates will impede the movement of the particles in the reactor, thus reduce the productivity of the entire system and may potentially lead to serious mechanical structure failure.

Structure Integrity and Strength Test (Fix Bed Test & Strength Test)

Based on the results from precious tests, combinations which demonstrated decent reactivity and recyclability were put in to fix bed reactor for structure integrity test and followed by strength test. The results are summarized in the following graph. (Figure 19)

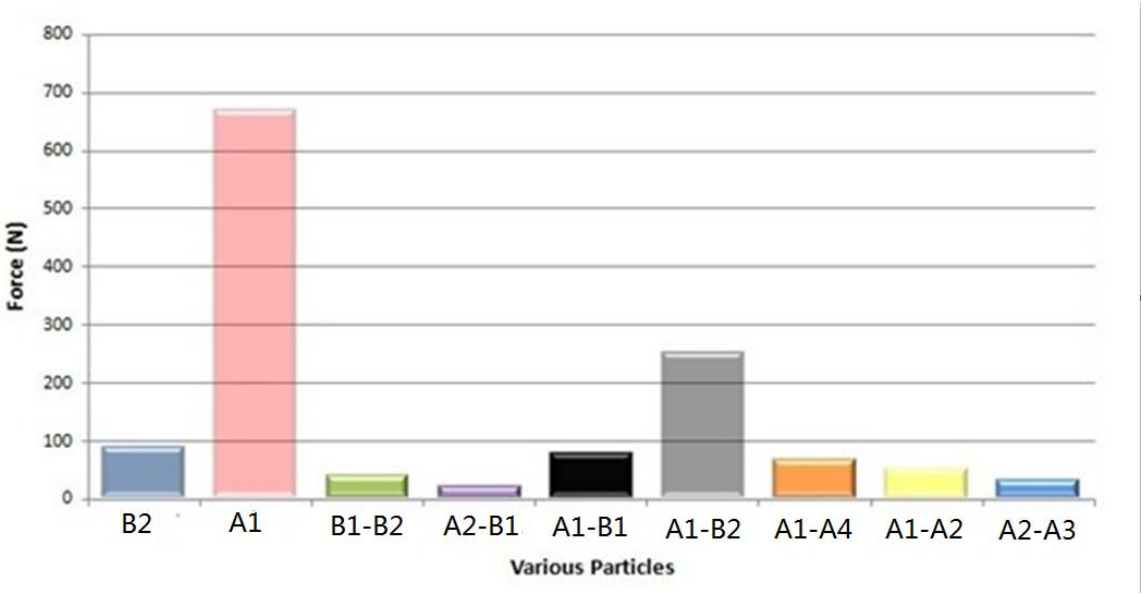

Figure 19: Average Particle Strength (fresh)

The A1 support provides the strongest particle strength for fresh particles. This is because Ti itself is a very strong metal, so it helps to stabilize and strengthen the pellets internal structure when mixed with Fe_2O_3. However, it should be also notice that, when

other supports were mixed with Ti and added into the particles, the particle strength decreased significantly (from 670 N for pure A1 support to averaged 100 N for other A1 mixed support. This is probably because the newly added support material breaks the internal structure Ti forms, and thus the particle strength decreased dramatically.

Therefore we conclude that A1 is the best support in terms of reactivity, recyclability and particle strength.

Conclusions and Recommendations

Particle Making and Pelletization

The scaled up process has proven to be effective in producing large amounts of pellets within a reasonable timeframe. With the addition of the magnesium stearate, the pellet production rate has increased from the order of ~$gday^{-1}$ to $kghour^{-1}$, and better mixing was achieved. No agglomerates were formed during mixing, this helps tremendously for the following pelletization step. The pellets have shown reactivities similar to the previously produced pellets from the dry-mixing process. This new method is also cost effective in terms of raw materials used. Preciously when corn starch solution was sprayed to help mixing, there is a waiting time for the mixed particles to be dried in oven overnight, followed by pelletization. With the new method, pelletization can start immediately after the mixing.

The scaled up process is currently limited by the size of the mixing drum. The maximum manageable amount of powder is approximately 2 kg. A larger mixer of a style other than a rotary drum would be preferred. With the drum mixer shown in **Error! Reference source not found.**, the larger particles would float to the top of the finer particles. This caused problems with mixing which required human intervention to manually break the agglomerated particles. Larger grinding media greater than ½" diameter would also help with the breaking of the particles because the ½" media could not always supply enough force to break the agglomerates.

For the bench top small pelletizer, the feeding of particle powder to the hold on the platform is arbitrary and solely determined by the person performing the pelletization.

Unlink the big pelletizer for scale up process, the bench top pelletizer thus have a inconsistent feeding problem, meaning the pellets produced may have density difference. This may influence the OC capacity and therefore influence the results from TGA test.

For better mixing of powders, methods other than the mechanical mixing may be considered. For example, we can dissolve the various powders into a solvent, and evaporate the solvent after complete mixing, such that each pellet is supposedly to have better mixing ratio as expected.

The geometry of the pellets also plays an important role in the actual SCL reactor. The current cylindrical pellets have angle, this will impede gas movement and increase the resistance in the reactor columns. Even worse, they can form a 'ring-like" structure at certain point of the column reactor, decrease the inner diameter of the column, and impede the continuous movement of particles. One possible solution to this is to use pellets with alternative geometry. For example, spherical structure will reduce the flow resistance to minimum and reduce the chance of forming the above mentioned "ring-like" layer. However, this will involve different pelletizing methods.

Reactivity and Recyclability

For reactivity and recyclability test, 1 pellet is not enough to obtain an accurate data for a specific combination of support materials. Multiple pellets may be needed. This, without question, will increase the experiment time. Possible solution is to use multiple TGAs to perform the tests.

Moreover, in order to improve the efficiency of reactivity rest, thermodynamic studies may be applied to each individual sample (base-support) before conducting the

TGA test. The redox kinetics has a close relationship with the materials thermodynamic properties. A thermodynamic analysis prior to the actual TGA test will provide a theoretical foundation to identify suitable support mixture, thus reduce experiment time.

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